Reactive intermediates revealed in secondary organic aerosol formation from isoprene

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Isoprene is a significant source of atmospheric organic aerosol; however, the oxidation pathways that lead to secondary organic aerosol (SOA) have remained elusive. Here, we identify the role of two key reactive intermediates, epoxydiols of isoprene (IEPOX = β-IEPOX + δ-IEPOX) and methacryloylperoxynitrate (MPAN), which are formed during isoprene oxidation under low- and high-NO_x conditions, respectively. Isoprene low-NO_x SOA is enhanced in the presence of acidified sulfate seed aerosol (mass yield 28.6%) over that in the presence of neutral aerosol (mass yield 1.3%). Increased uptake of IEPOX by acid-catalyzed particle-phase reactions is shown to explain this enhancement. Under high-NO_x conditions, isoprene SOA formation occurs through oxidation of its second-generation product, MPAN. The similarity of the composition of SOA formed from the photooxidation of MPAN to that formed from isoprene and methacrolein demonstrates the role of MPAN in the formation of isoprene high-NO_x SOA. Reactions of IEPOX and MPAN in the presence of anthropogenic pollutants (i.e., acidic aerosol produced from the oxidation of SO_2 and NO_2, respectively) could be a substantial source of "missing urban SOA" not included in current atmospheric models.

acid-catalyzed particle-phase reactions | epoxides | methacryloylperoxynitrate | organosulfates

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the most abundant nonmethane hydrocarbon emitted into the Earth's atmosphere, with emissions estimated to be 440–660 $TgC\,yr^{-1}$ (1). The atmospheric hydroxyl (OH) radical-initiated oxidation of isoprene, so-called photooxidation, plays a key role in establishing the balance of hydrogen oxide ($HO_x = OH + HO_2$) radicals in vegetated areas (2, 3) and influences urban ozone formation in populated areas blanketed with biogenic emissions (4). Formation of low-volatility compounds during isoprene oxidation has been estimated to be the single largest source of atmospheric organic aerosol [i.e., secondary organic aerosol (SOA)] (5–8).

The photooxidation of unsaturated volatile organic compounds (VOCs) proceeds through formation of a hydroxy peroxy (RO_2) radical, the fate of which depends on the concentration of nitrogen oxides ($NO_x = NO + NO_2$). Higher SOA yields from isoprene are observed under low-NO_x (or NO_x-free) conditions; in this regime, RO_2 radicals react primarily with HO_2, a pathway that tends to produce lower-volatility oxidation products than that involving the reaction of RO_2 with NO (9–11). Under high-NO_x conditions, RO_2 radicals react with NO to produce alkoxy (RO) radicals, or as a minor pathway, organic nitrates ($RONO_2$). For small VOCs ($\leq C_{10}$), like isoprene, these RO radicals generally fragment into smaller more volatile products, resulting in small amounts of SOA (9–11). Despite the fact that SOA from isoprene has been extensively studied (8), the chemical pathways to its formation under both low- and high-NO_x conditions have remained unclear. In this study we examine the mechanism of isoprene SOA formation in these two limiting regimes.

Results and Discussion

Isoprene SOA Formation under Low-NO_x Conditions: Role of Aerosol Acidity. Formation of SOA from the photooxidation of isoprene under low-NO_x conditions is enhanced in the presence of acidified sulfate seed aerosol over that in the presence of neutral aerosol (12); this is not observed under high-NO_x conditions because the aerosol phase is likely acidic enough due to the formation and presence of nitric acid (HNO_3) (13) and/or organic acids (12). The effect of increasing aerosol acidity on both gas- and aerosol-phase composition provides a critical clue to the chemical mechanism of SOA formation from isoprene under low-NO_x conditions. Enhancement of isoprene SOA mass with increasing aerosol acidity observed in laboratory chamber studies (12, 14, 15), including increased mass concentrations of the 2-methyltetrols (14, 15), organosulfates of isoprene (i.e., hydroxy sulfate esters) (15), and high–molecular weight (MW) SOA constituents (15), has been explained by acid-catalyzed particle-phase reactions. Although a linear correlation between the SOA mass formed and measured aerosol acidity (i.e., $nmol\,H^+\,m^{-3}$) has been found under dry conditions [approximately 30% relative humidity (RH)] (15), the actual acid-catalyzed particle-phase reactions responsible for these observed enhancements in isoprene SOA formation remain unclear, especially because previously proposed reactions, like that of organosulfate formation by alcohol sulfate esterification (16–18), appear to be kinetically unfavorable at atmospheric conditions (19).

Shown in Fig. 1*A–F* are the chemical ionization mass spectrometry (CIMS) (see *Materials and Methods*) time traces for selected ions corresponding to the important gas-phase products formed from the photooxidation of 49 and 40 ppb of isoprene in the presence of neutral and highly acidified sulfate seed aerosol, respectively. The SOA mass yields from isoprene were 1.3 and 28.6% for the neutral and highly acidified sulfate seed aerosol experiments, respectively. Under the conditions of these experiments, the RO_2 radicals formed react primarily with HO_2. In addition to the formation of hydroxycarbonyls, methyl-butenediols, hydroxyhydroperoxides (ISOPOOH), methacrolein (MACR), and methyl vinyl ketone (MVK), all of which are first-generation gas-phase oxidation products (Fig. 1*A–D*), we also observe the formation of second-generation epoxydiols of isoprene (IEPOX), as indicated in Fig. 1*F* (i.e., 9 and 0.6 ppb of IEPOX was measured in the neutral and acidic cases, respectively). Although the 2-methyltetrols (Fig. 1*E*) can be produced from RO_2 radical-cross reactions, their formation through this route is of minor

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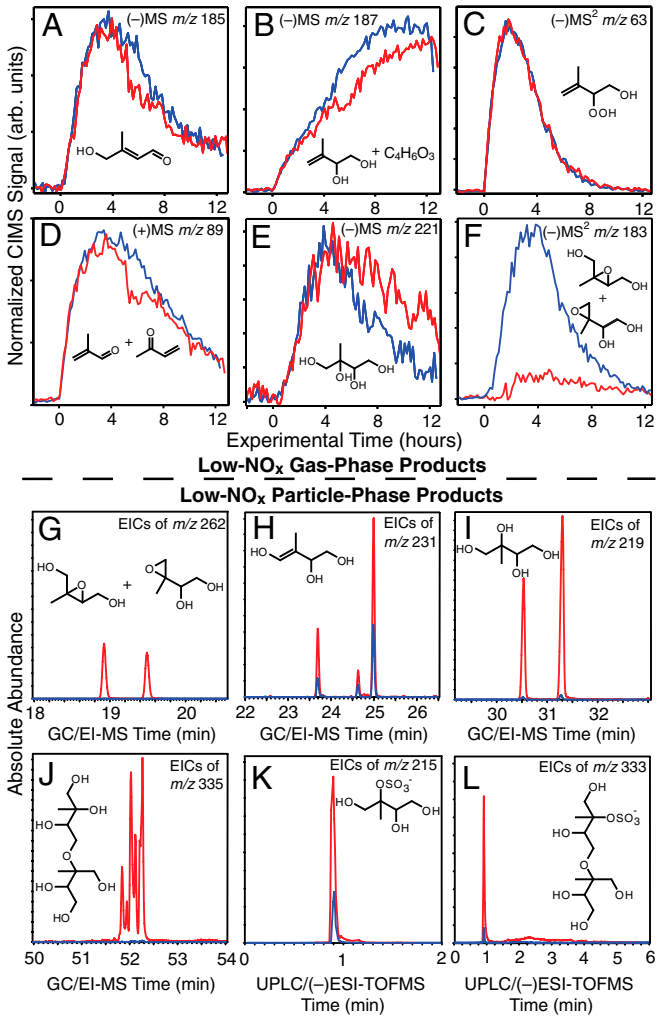

Fig. 1. Comparison of important gas- and particle-phase products produced from isoprene under low-NO_x conditions in the presence of either neutral (blue lines) or highly acidified (red lines) sulfate seed aerosol. In most cases, only one structural isomer is shown.

significance (approximately 0.2 ppb) in these experiments owing to the dominant $RO_2 + HO_2$ pathway. The hydroxycarbonyls (approximately 0.8 ppb) and methyl-butenediols (approximately 0.8 ppb) are first-generation products also formed from RO_2 radical-cross reactions; however, part of the CIMS signal associated with the methyl-butendiols (Fig. 1*B*) arises from later-generation oxidation products with the elemental composition $C_4H_6O_3$, likely a C_4-hydroxydicarbonyl and/or C_4-acid. Hydroxynitrates of isoprene were also observed (<0.1 ppb). Their formation results from background NO in the chamber. Thus a fraction of the MACR and MVK produced results from $RO_2 + NO$ reactions (approximately 3% of RO_2 radicals reacted with NO).

IEPOX (i.e., δ-IEPOX) was proposed to form from the photooxidation of isoprene under low-NO_x conditions in order to tentatively explain the formation of chemically characterized SOA constituents (12, 20). Gas-phase IEPOX (β-IEPOX and δ-IEPOX) was recently shown to form in substantial yields (upward of 75%) from the further oxidation of ISOPOOH (approximately 12 ppb measured in both the neutral and acidic cases in Fig. 1*C*) by OH under low-NO_x conditions (3). The substantial reduction of gas-phase IEPOX in the presence of highly acidified sulfate seed aerosol (Fig. 1*F*) confirms the role of IEPOX in the enhancement of isoprene SOA mass under lower-NO_x conditions at increased aerosol acidity.

Isoprene low-NO_x SOA was analyzed offline by gas chromatography/electron ionization–quadrupole mass spectrometry (GC/EI-MS) with prior trimethylsilylation and ultra performance liquid chromatography/electrospray ionization-time-of-flight mass spectrometry operated in the negative ion mode [UPLC/(–) ESI-TOFMS] (see *Methods and Materials*). Particle-phase IEPOX is characterized here using GC/EI-MS. The GC/EI-MS mass spectra of the trimethylsilyl (TMS)-derivatives of IEPOX associated with the two chromatographic peaks in Fig. 1*G* are shown in Fig. S1. Extracted ion chromatograms (EICs) of selected ions corresponding to particle-phase IEPOX, as well as the previously characterized C_5-alkene triols (20), 2-methyltetrols (5), hemiacetal dimers (12), organosulfate derivatives of the 2-methyltetrols (16, 17), and organosulfate derivatives of the hemiacetal dimers (18) are shown in Fig. 1*G–L*, respectively. Mass spectra in the present study for the previously characterized low-NO_x SOA constituents shown in Fig. 1*H–L* correspond to those collected in prior work (5, 12, 16, 20), and are shown in Fig. S1 and S2. The abundances of all low-NO_x SOA constituents shown in Fig. 1*G–L* are enhanced significantly in the presence of acidified sulfate seed aerosol. Using a suitable surrogate standard (i.e., *meso*-erythritol to quantify the 2-methyltetrols), we estimate that the mass concentrations of these compounds increased from 0.1 $\mu g\,m^{-3}$ for the neutral case to 5.1 $\mu g\,m^{-3}$ for the highly acidic case, corresponding to approximately 10 to 20%, respectively, of the total SOA mass formed.

Identification of IEPOX as the Intermediate Responsible for Acid-Enhanced Isoprene SOA. We hypothesize that particle-phase reactions of IEPOX play a significant role in the formation of the other major low-NO_x SOA constituents shown in Fig. 1*H–L*, as well as in the enhancement of total SOA mass. To test this hypothesis, we synthesized 2,3-epoxy-1,4-butanediol (BEPOX) (see *Materials and Methods*), which is the butadiene derivative of IEPOX, and conducted reactive uptake experiments in the presence of both neutral and highly acidified sulfate seed aerosol. BEPOX is used in these experiments instead of IEPOX because precursors for IEPOX are not commercially available. In these dark and dry (<10% RH) experiments, no OH precursor (e.g., H_2O_2) or NO_x was present; thus, only reactive uptake of BEPOX onto seed aerosol occurred. Two variations of these reactive uptake experiments were carried out: (*i*) BEPOX was added first, followed by the injection of seed aerosol; or (*ii*) seed aerosol was added first, followed by the injection of BEPOX. CIMS time traces corresponding to version (*i*) of the BEPOX reactive uptake experiments are shown in Fig. 2*A*. The only parameter varied was the acidity of the sulfate seed aerosol. BEPOX is rapidly removed from the gas phase within the first hour after the acidified sulfate seed aerosol is injected into the well-mixed chamber. Upon the injection of neutral sulfate seed aerosol, BEPOX disappears from

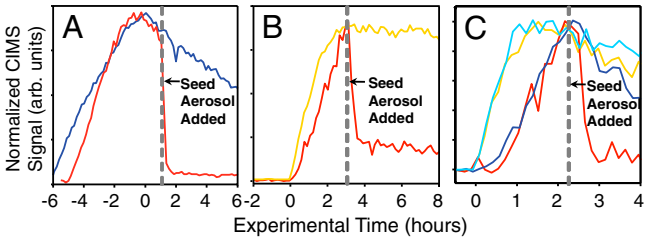

Fig. 2. CIMS time traces: (*A*) Reactive uptake of gas-phase BEPOX in the presence of either neutral (blue line) or highly acidified (red line) sulfate seed aerosol under dark conditions. (*B*) Hydroxy hydroperoxide (orange line) and BEPOX (red line) produced from butadiene under low-NO_x conditions. (*C*) ISOPOOH (neutral seed = light blue line; highly acidic seed = orange line) and IEPOX (neutral seed = blue line; highly acidic seed = red line) produced from isoprene under low-NO_x conditions. Signals of the IEPOX are normalized to that of the ISOPOOH when lights are turned off.

wall loss only and not reactive uptake. Once the injection of gas-phase BEPOX ended (indicated at time zero in Fig. 2*A*), it decayed at similar rates before either the neutral or highly acidified sulfate seed aerosol was injected. The clear conclusion is that BEPOX loss to the highly acidic seed aerosol results from acid-catalyzed particle-phase reactions.

SOA formed in the acidified BEPOX reactive uptake experiments shown in Fig. 2*A* was collected for offline chemical analyses by GC/EI-MS and UPLC/(−)ESI-TOFMS (Fig. S3). In addition to sharing similar retention times (RTs), the mass spectrum of the TMS-derivative of the particle-phase BEPOX (Fig. S3) corresponds exactly to that of the synthesized BEPOX standard (Fig. S4). The major chromatographic peak observed in the EIC of m/z 248 (Fig. S3) is attributable to particle-phase BEPOX, whereas the two later-eluting minor peaks represent BEPOX isomers. The other major SOA constituents characterized from the reactive uptake of BEPOX are also exact analogues of isoprene SOA formed under low-NO_x conditions (i.e., differing by a mass of 14 Da, which corresponds to a CH_2 group); these include: C_4-alkene triols, tetrols (i.e., threitol and erythritol), dimers, organosulfate derivatives of the tetrols, and organosulfate derivatives of the dimers (Fig. S3). Equivalent to the low-NO_x isoprene SOA (Fig. 1*G–L*), these BEPOX SOA constituents were significantly enhanced under increased seed aerosol acidity, consistent with the rapid removal of gas-phase BEPOX onto the highly acidified sulfate seed aerosol. The tetrols (i.e., threitol and erythritol) were quantified by GC/EI-MS and their summed mass was found to increase from 43 ng m^{-3} to 1.0 μg m^{-3} from neutral to highly acidic conditions.

In version (*ii*) of the BEPOX reactive uptake experiments, within the first hour after the addition of BEPOX, the sulfate aerosol mass concentration decayed more rapidly (by approximately 58% of its initial loading) in the highly acidic case than that which could be explained by wall loss alone, indicating depletion of the inorganic sulfate through chemical reaction with BEPOX (Fig. S5). A similar observation made in isoprene SOA formation (16) is consistent with the reactive uptake of IEPOX forming organosulfates of isoprene. The SOA mass generated after the injection of gas-phase BEPOX increased from 0.9 to 15.8 μg m^{-3} from neutral to acidified sulfate seed aerosol. Importantly, organosulfates of BEPOX (i.e., organosulfate derivatives of the tetrols and dimers, as well as higher order organosulfates shown in Fig. S6) were also characterized in these experiments (Fig. S3). We conclude from these observations that conversion of inorganic sulfate into organosulfates occurs by the acid-catalyzed ring opening of the epoxydiols followed by the subsequent nucleophilic addition of inorganic sulfate.

Reactive uptake onto acidified sulfate seed aerosol also occurs when BEPOX and IEPOX are formed from butadiene and isoprene photooxidation, respectively. 100 ppb of butadiene and 50 ppb of isoprene were initially irradiated in the absence of seed aerosol (Fig. 2*B* and *C*, respectively). Once sufficient gas-phase levels of both BEPOX and IEPOX formed, seed aerosol was injected. For the butadiene experiment (Fig. 2*B*), only highly acidified sulfate seed aerosol was injected. Because hydroxyhydroperoxides and BEPOX, gas-phase oxidation products of butadiene, are isomers both detected by the CIMS technique at m/z 189, characteristic daughter ions produced from m/z 189 were used to differentiate between these two compounds. The daughter ions at m/z 63 and 169 are uniquely characteristic of the hydroxyhydroperoxide and BEPOX, respectively (3). Upon the injection of acidified sulfate seed aerosol, BEPOX was the only oxidation product rapidly removed from the gas-phase mixture (decayed by approximately 75% within the first hour after seed aerosol was injected). The SOA constituents from butadiene shown in Fig. 2*B* are precisely those shown in Fig. S3. In the case of isoprene photooxidation (Fig. 2*C*), as observed for the BEPOX reactive uptake and butadiene photooxidation (Fig. 2*A* and *B*, respectively), gas-phase IEPOX disappeared significantly only in the presence of acidified sulfate seed aerosol (Fig. 2*C*). Moreover, the constituents characterized in the SOA formed from the latter experiment are precisely those shown in Fig. 1*G–L*.

Mechanism of Isoprene SOA Formation Under Low-NO_x Conditions. An updated chemical mechanism for SOA formation from isoprene under low-NO_x conditions is shown in Fig 3. The gas-phase formation of IEPOX has been fully characterized by Paulot et al. (3). Here we have established that the reactive uptake of IEPOX occurs by the acid-catalyzed ring opening of this epoxydiol, followed by the subsequent addition of the following nucleophiles: (*i*) H_2O, (*ii*) inorganic sulfate, (*iii*) a 2-methyltetrol

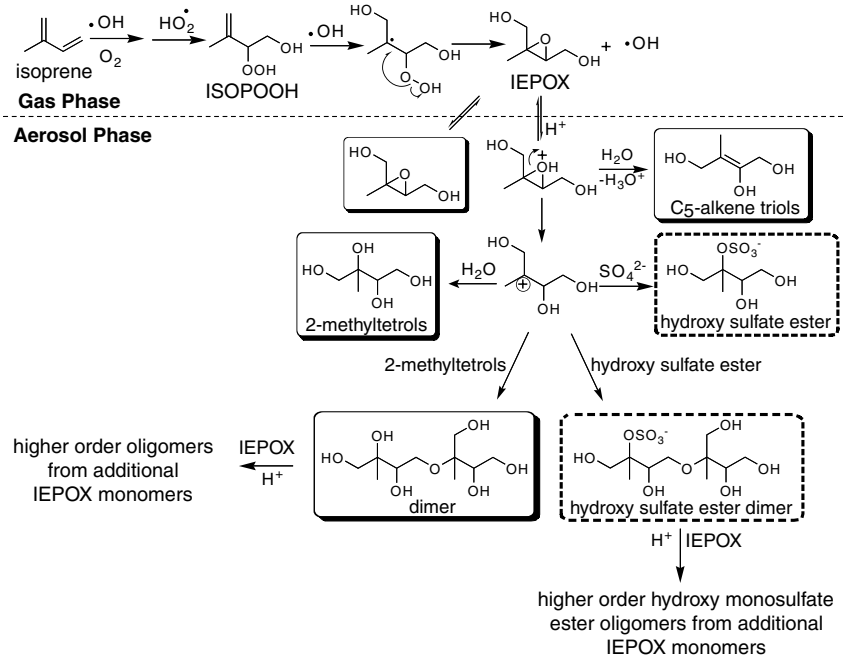

Fig. 3. Mechanism for the enhancement of SOA formation from isoprene under lower-NO_x conditions due to increased aerosol acidity. SOA constituents in shaded and dashed boxes are observed by GC/MS and UPLC/(−)ESI-TOFMS, respectively. Only the β-IEPOX is considered here, but this also applies to δ-IEPOX.

already formed in the aerosol, and (*iv*) a hydroxy sulfate ester already present in the aerosol. Unreacted particle-phase IEPOX observed in the isoprene SOA is likely a result of equilibrium gas-to-particle partitioning. Although the formation of 2-methyltetrols has been detected from the further oxidation of methyl-butenediols under conditions in which $RO_2 + RO_2$ reactions dominate (at large isoprene mixing ratios, i.e., 8–12 ppm C) (21), the atmospheric formation of the 2-methyltetrols will occur primarily via the further reaction of IEPOX as shown in Fig. 3, because the HO_2 concentration exceeds that of all RO_2 radicals (22) and because rate coefficients of $RO_2 + RO_2$ reactions are usually smaller than those for $RO_2 + HO_2$ reactions (23). The organosulfates of isoprene are shown conclusively to form from the reactive uptake of IEPOX, rather than by the previously proposed alcohol sulfate esterification mechanism (18). This conclusion is consistent with recent work by Iinuma et al. (24), who showed organosulfates of α- and β-pinene form through the reactive uptake of α- and β-pinene oxides only in the presence of acidified sulfate seed aerosol. Additionally, recent work has shown that organosulfate formation is kinetically favorable only for epoxides and not for alcohols at atmospherically relevant conditions (19).

Although the C_5-alkene triols were observed in these experiments, their exact formation mechanism remains unclear. We cannot rule out the possibility that these compounds are produced from the trimethylsilylation step prior to GC/EI-MS analysis because a TMS-derivative of the synthesized BEPOX standard was found to have a contribution from C_4-alkene triols. Preliminary results suggest that these compounds are more abundant than the tetrols under high RH conditions. Enhanced C_5-alkene triol concentrations have been observed when transitioning from the dry to wet seasons in the Amazon (20). Finally, the dimers previously observed in both laboratory-generated isoprene SOA and organic aerosol collected from the Amazon are likely not a result of hemiacetal formation (12); rather, these dimers are shown to form from polymerization of IEPOX by acid-catalyzed ring opening of IEPOX.

Isoprene SOA Formation under High-NO_x Conditions: Role of MPAN. The majority of the high-NO_x SOA yield from isoprene has previously been traced to the oxidation of a major [25% yield (25)] first-generation oxidation product of isoprene, MACR (9, 12). Providing further evidence of the role of MACR, the chemical composition of the SOA produced in the oxidation of MACR is similar to that found in studies of the oxidation of isoprene, especially 2-methylglyceric acid (2-MG), a C_4-dihydroxycarboxylic acid, which undergoes esterification to produce low-volatility oligoesters (12, 26). Both 2-MG and its corresponding diester have been observed in ambient aerosol samples (7).

The preservation of the four-carbon backbone in the SOA produced following the oxidation of MACR provides significant constraints on the gas-phase mechanism that yields the SOA precursor. Oxidation of MACR by OH proceeds both via addition to the double bond (approximately 55%) and abstraction of the aldehydic hydrogen (45%) (27, 28). Preservation of the carbon backbone generally precludes formation of RO radicals because they rapidly decompose to form hydroxyacetone (via OH addition) and methylvinyl radicals (via aldehydic abstraction) (28). This suggests that, following abstraction of the aldehydic hydrogen by OH, formation of MPAN is likely key to SOA production. MPAN is formed from MACR with a maximum yield of approximately 45% (27, 29). Following addition of OH to the double bond, the only known gas-phase mechanism that prevents C-C fragmentation in the presence of NO_x is the channel leading to the formation of a hydroxynitrate (7, 27, 30). Thus, to oxidize both the double bond and the aldehydic hydrogen, one route to C_4 preservation leads to the formation of the hydroxynitrate of MPAN. Alternatively, the addition of OH to MPAN might lead to the formation of bridged oxygen compounds if the alkyl radical (or subsequent RO_2 or RO radicals) rearrange unimolecularly and decompose by breaking off the weak peroxynitrate moiety forming peroxy or epoxy carbonyls.

To test the hypothesis that the formation of MPAN is key for SOA formation, 277 ppb MACR was oxidized by OH (formed via HONO photolysis) in the presence of a very high concentration of NO (>500 ppb). Under these conditions, the peroxyacyl radical formed following H-abstraction (and addition of O_2) reacts primarily with NO to form formaldehyde, CO, and CO_2 rather than with NO_2 to form MPAN (27, 29). Although formation of hydroxynitrate was observed from the addition channel (approximately 10–15% of hydroxyacetone), little SOA was produced (mass yield <2%). SOA yields (2.9% from 257 ppb MACR) were higher when 290 ppb of NO was added, and highest (5.1% from 285 ppb MACR) when 350 ppb of additional NO_2 (instead of NO) was injected. As shown in Fig. S7, the relative aerosol-phase concentrations of oligoesters are also enhanced under higher $[NO_2]/[NO]$ ratios, consistent with the trends observed in SOA yields from MACR photooxidation. The RTs and molecular formulas match those of the oligoester products formed in isoprene high-NO_x SOA. NO levels remained above 120 ppb during the course of all the experiments, and thus $RO_2 + HO_2$ and $RO_2 + RO_2$ reactions are not competitive. HONO levels, as measured by CIMS, were within 15% among these experiments. The observed increase in SOA at higher NO_2 levels is also unlikely to be a result of condensation of nitric acid from $OH + NO_2$ reactions because addition of gas-phase nitric acid did not lead to additional aerosol growth. The observed effect of $[NO_2]/[NO]$ ratio on oligoester formation and overall aerosol yields in MACR photooxidation suggests the importance of peroxynitrate formation via an $RO_2 + NO_2$ pathway. In the chamber, the lifetime of MPAN against thermal decomposition is about 100 min (31) and can be effectively much longer under higher $[NO_2]/[NO]$ ratios because the peroxyacyl radicals formed following thermal decomposition react preferentially with NO_2 reforming MPAN.

Identification of MPAN as Key Intermediate in Formation of SOA from Isoprene and MACR. To verify the hypothesis that the route to high-NO_x SOA formation from isoprene goes through MPAN, experiments were carried out with synthesized MPAN (see *Materials and Methods*). When MPAN was injected into the chamber in the presence solely of ammonium sulfate seed, SOA was not observed. Significant aerosol growth was observed only upon photooxidation of MPAN (with photolysis of HONO used as the OH source). Moreover, as shown in Fig. 4, the composition of SOA formed from MPAN oxidation was similar to that from high-NO_x photooxidation of MACR and isoprene. In particular, 2-MG and its corresponding oligoesters are identified in all three aerosol samples using both GC/EI-MS and UPLC/(−)ESI-TOFMS. Detailed chemical characterization of 2-MG and its corresponding oligoesters (12, 26) and similar analysis of the current samples confirm the presence of these products in aerosol formed from MPAN oxidation (Fig. 4 and Table S1). Other aerosol components found in isoprene SOA, such as compounds with a C_5-hydroxynitrate backbone, are not found in MACR or MPAN SOA, but their contribution to total aerosol mass is likely small, and their formation mechanisms have been tentatively established (18). We confirmed that 2-MG and its corresponding oligoesters are formed as a result of MPAN oxidation and not an impurity (i.e., methacrylic acid) (*SI Text*).

Additional experiments provide insight into the mechanism by which 2-MG is formed from the OH reaction of MPAN. Oxidation of 2-methyl-3-buten-2-ol (MBO), structurally similar to isoprene but lacking the second double bond, leads to no aerosol formation. This suggests that formation of 2-MG requires OH reaction with the double bond of MPAN. OH addition to the MPAN double bond, followed by addition of O_2, leads to forma-

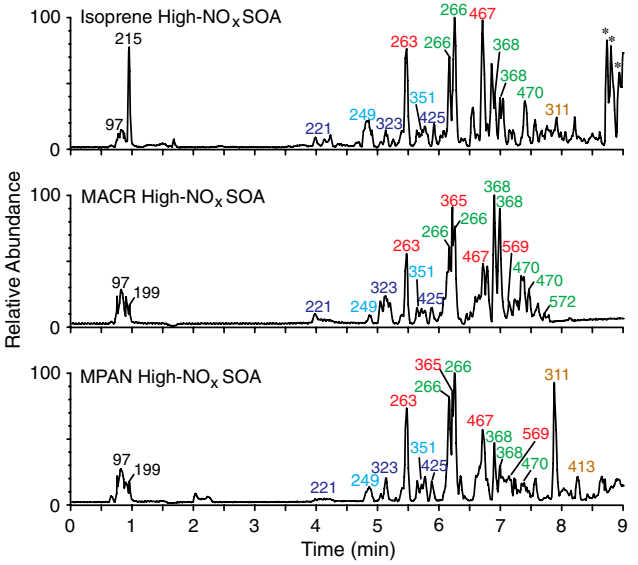

Fig. 4. UPLC/(−)ESI-TOFMS BPCs. The numbers listed above each peak correspond to the respective $[M-H]^-$ base peak ions. Similar-colored $[M-H]^-$ ions are of the same oligoester series (Table S1). m/z 97, 199, and 215 correspond to sulfate, an organosulfate of 2-MG (16), and an organosulfate of 2-methyltetrols (15, 16), respectively.

tion of an RO_2 radical; under the chamber conditions, reaction with NO is most likely, leading to formation of either an RO radical or a C_4-hydroxynitrate peroxyacyl nitrate (PAN). Owing to the 2-position of the alkoxy group, this C_4-alkoxy radical is unlikely to undergo traditional H-atom transfer isomerization and therefore decomposes rapidly to break the C_4-backbone. One possibility is that 2-MG is formed through the C_4-hydroxynitrate-PAN channel (see Fig. 5). Dommen et al. (32) observed lower-volatility isoprene SOA (which is consistent with the formation of oligomers) to form under dry rather than humid conditions, which is consistent with a mechanism that involves decomposition of the C_4-hydroxynitrate-PAN into 2-MG and allows for subsequent esterification of 2-MG into the observed oligoesters. We do not, however, have conclusive chemical evidence to support the hypothesis that the C_4-hydroxynitrate-PAN is the main precursor to the isoprene high-NO_x SOA. Indeed, there is some evidence that this is not the route. A signal, comparable

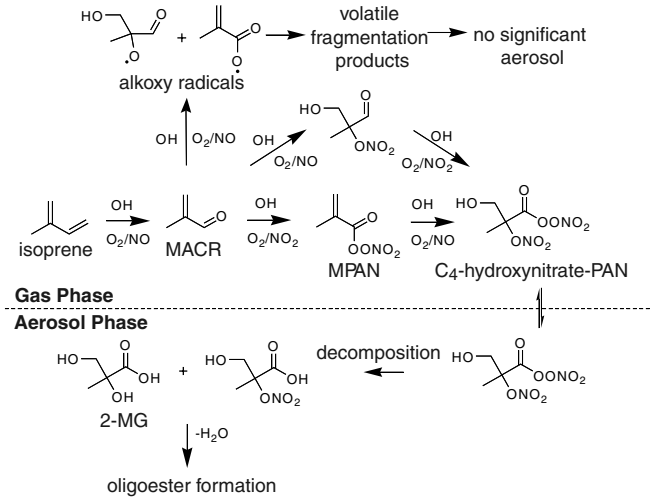

Fig. 5. Possible chemical mechanism for the formation of isoprene SOA under high-NO_x conditions. Detailed chemical structures of the high-NO_x SOA constituents resulting from the oligoester formation can be found in Table S1.

in magnitude to the hydroxynitrate of MACR (at m/z 234) and highly correlated to the time trace of SOA formation, is observed at m/z 311: a mass consistent with the cluster of CF_3O^- with the C_4-hydroxynitrate-PAN. Assuming the same CIMS response factor as glycolaldehyde, the signal at m/z 311 is consistent with all of the C_4-hydroxynitrate-PAN being accounted for in the gas phase (assuming the yield of the C_4-hydroxynitrate from MPAN is comparable to the yield of the hydroxynitrate from MACR), and as a result, this compound could not be the SOA precursor. Thus, it is possible that some unknown C_4-preserving chemical reaction is occurring when MPAN is oxidized by OH (e.g., similar to the formation of IEPOX under low-NO_x conditions, the OH-MPAN radical adduct intramolecularly rearranges into a highly strained epoxide before O_2 adds).

The OH reaction rate constants of saturated PANs are sufficiently small ($<1\times10^{-13}$ $cm^3\,mol^{-1}\,s^{-1}$) that the major sink for these compounds in the atmosphere is thermal decomposition to the peroxyacyl radical followed by reaction with NO and subsequent decomposition to CO_2. By contrast, the OH reaction of MPAN is competitive with thermal decomposition (28). Here we confirm that MPAN is the key intermediate in the isoprene and MACR systems in the formation of 2-MG and its corresponding low-volatility oligoesters in the aerosol phase. If a PAN-type compound is involved in the formation of aerosol-phase products, the aerosol yields should depend on the $[NO_2]/[NO]$ ratio because this ratio determines whether the peroxyacyl radicals produced via thermal decomposition reform PANs or react with NO and decompose. With urban $[NO_2]/[NO]$ ratios typically around 7, SOA mass yields from isoprene and MACR previously measured at $[NO_2]/[NO]$ ratios around 1 could be underestimated (8). Experimentally, such high $[NO_2]/[NO]$ ratios are not achieved using HONO as an OH source, because NO is produced from both the synthesis of HONO and photolysis of HONO with UV irradiation.

Atmospheric Implications. The importance of IEPOX and MPAN in forming isoprene SOA under low- and high-NO_x conditions, respectively, provides significant insights into heretofore-unidentified aerosol precursors. In the presence of anthropogenic pollutants, such as NO_2 and acidic aerosol produced from the oxidation of SO_2, SOA mass yields from isoprene under high- and low- NO_x conditions, respectively, increase substantially. Because isoprene is estimated to be the largest single contributor to global SOA, these results may help to resolve two existing dilemmas in atmospheric chemistry: (*i*) Radiocarbon (^{14}C) data consistently indicate that well over half of the ambient SOA is of modern (biogenic) origin (7, 33), whereas correlations between water-soluble organic carbon and anthropogenic tracers, such as CO, suggest that much of the SOA is actually of anthropogenic origin (34, 35); and (*ii*) comparisons between measured and predicted SOA based on known precursors suggest that there is a substantial amount of "missing urban SOA" not included in current models (35–37). Revising the chemistry of isoprene in regional and global SOA models could lead to a decrease in this discrepancy; however, the measurement and parameterization of aerosol acidity requires additional work.

Materials and Methods

Experimental Details. The experiments were carried out in the Caltech dual 28-m^3 fluorinated ethylene propylene Teflon chambers (38). Seed aerosol is generated using a constant rate atomizer. Dilute solutions (concentrations of 0.06 M or lower) of ammonium sulfate and magnesium sulfate with sulfuric acid are used for neutral and highly acidic seed aerosol, respectively. The particle number and volume concentrations are corrected for particle wall loss using size-dependent coefficients determined from loss of inert particles. Isoprene, MACR, or MBO is added to the chamber by vaporizing a known volume of the hydrocarbon in a glass bulb. In the reactive uptake experiments (Table S2 and *SI Text*), BEPOX is injected into the chamber by vaporizing a small (approximately 30 mg) amount of the solid at approximately 60 °C

in a small glass vial and introducing the vapor into the chamber in a stream of N_2. The amount injected into the chamber is estimated by measuring the mass loss of BEPOX after injection. MPAN is injected in a similar manner in a −10 °C ice-salt bath. At −10 °C, dodecane has a negligible vapor pressure, and as a result, is not expected to be introduced into the chambers. In low-NO_x photooxidation experiments (Table S2 and *SI Text*), the photolysis of H_2O_2 is used to generate OH radicals. In order to prevent partitioning of H_2O_2 into the seed aerosol, all low-NO_x experiments were conducted under dry conditions (<10% RH). At the relatively high mixing ratios of H_2O_2, significant HO_2 radical levels are produced by the OH + H_2O_2 reaction, which is favored at the slow chamber photolysis rate of H_2O_2. In high-NO_x photooxidation experiments, the photolysis of nitrous acid (HONO) is used as the OH precursor (see Table S3 and *SI Text*).

Gas-Phase Measurements. The concentrations of isoprene, MACR and MBO are monitored by a gas chromatograph equipped with a flame ionization detector (GC/FID, Agilent 6890N). NO/NO_x and O_3 are monitored by commercial chemiluminescence monitors (Horiba, APNA 360 and APOA 360, respectively). A custom-modified Varian 1200 CIMS was used to continuously monitor gas-phase species (3) (*SI Text*).

Aerosol-Phase Measurements. Aerosol size distributions and volume concentrations are measured using a differential mobility analyzer (TSI, Inc.,3081) with a condensation nuclei counter (TSI, Inc., 3760). Aerosol samples are collected onto Teflon filters for offline chemical characterization by both GC/EI-MS with prior trimethylsilylation and UPLC/ESI-TOFMS. Filter handling and extraction protocols in high-purity methanol have been described previously for aerosol samples analyzed by the UPLC/(−)ESI-TOFMS technique (18). Details of the sample preparation and operation protocols for the GC/EI-MS technique can be found in the *SI Text*. Selected SOA samples formed from the reactive uptake of BEPOX on either neutral or acidified sulfate seed aerosol were continuously sampled by a particle-into-liquid sampler with subsequent offline analysis by ion chromatography (39).

Materials

Isoprene (Aldrich, 99%), MACR (Aldrich, 95%), and MBO (Aldrich, 98%) are obtained from commercial sources. BEPOX is synthesized following the procedure derived by Skinner et al. (40) (*SI Text*). MPAN is synthesized from methacrylic anhydride (Aldrich, 94%) in dodecane (Sigma-Aldrich, 99 + %, anhydrous) based on the method of Nouaime et al. (41) with a few modifications (*SI Text*). The purity of the product is confirmed by gas-phase FTIR spectroscopy (*SI Text*).

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